

Use of Waste Energetic Materials as a Fuel Supplement In Utility Boilers

Craig A. Myler

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, Maryland

William M. Bradshaw

Oak Ridge National Laboratory
Operated by Marin Marietta Energy Systems, Inc.
for the U.S. Department of Energy under contract
No. DE-AC05-84OR21400

Michael G. Cosmos

Weston Services, Inc.

West Chester, Pennsylvania

ABSTRACT

Waste energetic material produced during the manufacture of explosives has been considered a by-product waste which must be disposed of. Methods such as open burning or open detonation pose potential environmental risks while disposal in specially designed hazardous waste incinerators is costly. No current method capitalizes on these materials inherent energy capacity. Efforts to utilize these wastes as supplements to fuel oil are under way. Laboratory and bench scale operations verify the principle while economic analysis shows a positive advantage using this approach. Pilot scale testing is in progress to develop fuel mixing/feeding procedures and to determine fuel mixture energy parameters.

Introduction

Production and stockpiling of explosives by the U.S. Army results in the generation of waste energetic materials. Typically, these materials contain nitrated aromatic compounds which are classified as hazardous due to their inherent reactivity. Environmentally safe

Report Documentation Page			<i>Form Approved OMB No. 0704-0188</i>	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE AUG 1990	2. REPORT TYPE	3. DATES COVERED 00-00-1990 to 00-00-1990		
4. TITLE AND SUBTITLE Use of Waste Energetic Materials as a Fuel Supplement in Utility Boilers		5a. CONTRACT NUMBER		
		5b. GRANT NUMBER		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)		5d. PROJECT NUMBER		
		5e. TASK NUMBER		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD, 21010		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES See also ADA235005, Volume 1. Minutes of the Explosives Safety Seminar (24th) Held in St. Louis, MO on 28-30 August 1990.				
14. ABSTRACT see report				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 22
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	19a. NAME OF RESPONSIBLE PERSON	

methods are used to dispose of these materials as hazardous wastes; however, they do not take advantage of the energy content of these materials. A program initiated by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) in conjunction with Oak Ridge National Laboratory (ORNL) and Roy F. Weston, Inc. is investigating the use of these waste materials as a supplement to fuel oil for use in standard industrial-type boilers. Using the energy stored in these wastes reduces fuel consumption while eliminating potential hazardous waste. Each of these benefits is a national priority item. The development of this technology is therefore highly desirable.

Nature of the Waste

To effectively treat the subject, a description of the nature of the wastes as well as their origin is in order. Energetics are separated into three classes:

(1) Propellants

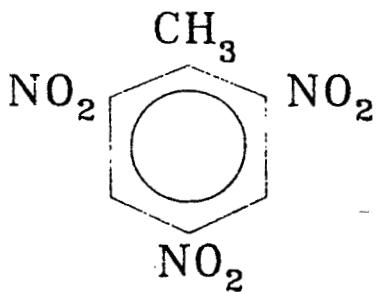
(2) Explosives

(3) Pyrotechnics

Propellants and pyrotechnics will not be included in this report. This does not preclude their use as fuel supplements and work has been initiated to investigate the use of propellants as fuel supplements, either as admixtures to fuel oils or as supplements to coal.

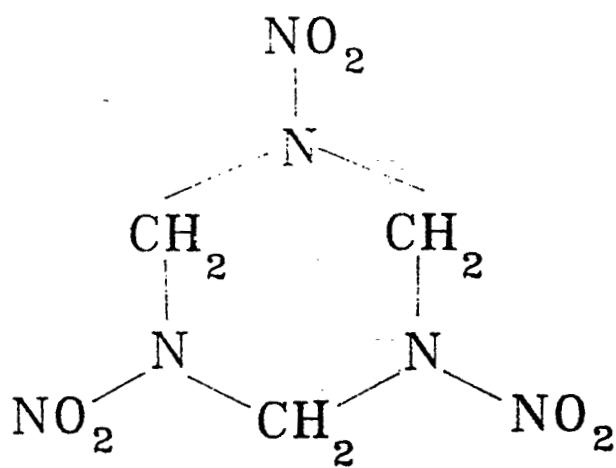
The two primary explosive wastes of concern are trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX). These are the most prevalent explosives in use today and constitute the greatest inventory of waste. The structures of these compounds along with pertinent physical data are given in Figures 1 and 2. Of particular note is the substantial amount of available nitrogen. This will be discussed in terms of expected combustion products later in this report. TNT and RDX are often combined (normally with a small amount of paraffin) to form a composite explosive. The most common is Composition B or simply, Comp B, which is a 40% TNT to 60% RDX mixture.

As class A explosives, both TNT and RDX constitute a reactivity hazard. Handling, storage and use require special care and attention to insure the safety of personnel. In addition to its reactivity, TNT also constitutes a toxicity hazard. The American Conference of Governmental Industrial Hygienists recommends a Time Weighted Average (TWA) maximum concentration of 0.5 mg/m^3 and indicates a dermal hazard with TNT.¹ The risk



Melting Point	80 to 81 °C
Color	Yellow, Crystalline
Boiling Point	345 °C
Density	1.654 gm/cm ³
Viscosity	0.139 poise at 85. °C
Specific Heat	251.8 J/mole-K at 27 °C
Heat of Combustion	809.18 to 817.2 kcal/mole
Solubility at 0 °C	57 gm/100 gm Acetone 28 gm/100 gm Toluene
Solubility at 50 °C	346 gm/100 gm Acetone 208 gm/100 gm Toluene

Figure 1: Structure and Physical Properties of Trinitrotoluene (TNT)²



Melting Point	202 to 203 °C
Color	White, Crystalline
Density	1.806 gm/cm ³
Specific Heat	1.277 J/mole·K at 20 °C
Heat of Combustion	501.8 to 507.3 kcal/mole
Solubility at 0 °C	4.2 gm/100 gm Acetone 0.016 gm/100 gm Toluene
Solubility at 50 °C	12.8 gm/100 gm Acetone 0.087 gm/100 gm Toluene

Figure 2: Structure and Physical Properties of Cyclotrimethylenetrinitramine (RDX)³

associated with this toxicity is generally small due to TNT being a solid under standard conditions as well as its low solubility in water. Even so, this toxicity cannot be ignored in any program utilizing TNT. Necessary precautions include safe explosives handling techniques, precaution against skin contact, and insurance against airborne contamination. Safe explosives handling including prevention against skin contact is commonly practiced and will not be discussed further.

The heating value of RDX is approximately 9 kJ/g while for TNT it is approximately 15 kJ/g. Each of these compounds burns easily and completely. The largest drawback to utilization as fuel supplements (outside of their reactivity) is the production of NOx. Combustion of these explosives produces some quantity of NOx above that which would be produced from the combustion of standard fuels. This NOx production was found to be approximately 0.54 g/MJ of fuel.⁴ Current test objectives include the characterization of these emissions and determination of means to curtail or treat the production of NOx.

Sources of the Waste

Along with the preceding discussion on the chemical nature of the waste, a brief description of the source of the waste and its physical state is in order. Two sources contribute to the inventory of waste explosives. The first of these is the normal production process. The second source is that inventory which becomes either obsolete due to its packaging or unserviceable due to storage, damage, etc.

As in the production of most items, especially in batch-produced chemicals, off specification materials are sometimes produced. Due to the military nature of explosives, strict production specifications are enforced. Batches of explosives sometimes fail to meet specifications which leads to their classification as wastes. Lackey⁵ provides an estimate of current energetic waste generation of 1.13×10^6 kg/yr. This estimate grows to 4.60×10^6 kg/yr during full scale production. It should be noted that no TNT is currently produced. Additionally, loading of munitions with explosives results in significant waste generation through equipment wash down procedures.

The second source of waste explosives is unserviceable stockpiles. If a weapon is no longer a part of the Army inventory, the munitions it uses may be classified as unserviceable or obsolete. Also, quality

control of stockpiled munitions may determine that a particular munition is unable to meet requirements for military service and it will be classified as unserviceable. This may be due to the breakdown of the explosive itself, degradation of other chemical portions of the munition such as a propellant charge, or to a deterioration of the munition body (for example a corrosion of the casing). Table 1 provides an estimate of the amount of unserviceable explosives in the current Army inventory.

TABLE 1: Estimate of Unserviceable Explosives Contained In U.S. Army Stockpile (1985)

	<u>COMP B (10⁶ kg)</u>	<u>TNT (10⁶ kg)</u>
Munitions	2.535×10^6	1.496×10^6
Reclaimed Material	2.315×10^6	----
Total	4.850×10^6	1.496×10^6

Finally, current disposal practices will be discussed. Two methods are generally used, not including continued storage which by its nature is expensive and non-productive. The first is destruction by open detonation of the explosives. This practice is simple, relatively safe and expedient. It has recently come under environmental scrutiny and testing is currently in

progress to determine the impact of this disposal method on the environment. Open detonation does not capitalize on the heating value of the explosives.

The second current method of disposal is by incinerating the waste explosives. Typically, the explosive is mixed to form a water-explosive slurry and fed to a rotary kiln. A fuel such as propane or fuel oil is used to maintain the kiln temperature at approximately 1200 °C. This process requires approximately 1.67 kg of fuel oil per kg of explosive destroyed. Although this process can be made environmentally acceptable, it is expensive in terms of capital cost and energy consumption.

Neither of the above disposal practices takes advantage of the energy contained in the explosives. With limited government resources a constant concern, a less costly alternative approach is desirable. In the case of mobilization for national defense, limited fuel reserves makes utilization of this energy source even more important.

Safety

Safety is of paramount importance in using explosives as fuel supplements. The very nature of explosives requires special handling during their intended use and even stricter controls during combustion in an industrial

boiler. Three separate areas of concern will be addressed. First, the rheology of explosives-fuel oil mixtures will be discussed. Second, physical properties with impact on compatibility of the explosives with fuel oils will be described. Finally, the likelihood of detonations occurring is addressed. These three safety related areas are fully described by Lackey.⁷

Due to the physical state of the waste explosives (irregularly sized solid pieces) and the relatively low solubility of TNT and RDX in fuel oils, a solvent is used to bring the TNT and RDX into solution. At some concentrations the RDX and TNT form slurries, especially upon removal of the solvent. Also, mixtures of toluene, TNT and fuel oil were shown to produce multiphase liquid mixtures which are undesirable for feed to a boiler. An optimum composition for the supplemented fuel must be determined and has an upper boundary dictated by detonation potential which will be described later.

Proper combustion of fuel oils is dependent on the burner systems ability to atomize the fuel. Viscosity is a key design parameter in selection of an atomizing nozzle and burner. Viscosity data for TNT supplemented fuel oils is given in Table 2. As shown, the viscosity of a No. 2 fuel oil supplemented with TNT does not show a significant increase in viscosity due to the addition of the explosive.

Explosives/Fuel Oil Compatibility

Consideration was given to the chemical compatibility of TNT and RDX with fuel oil.⁷ Differential thermal analysis, vacuum thermal stability and accelerating rate calorimetry all showed that neither TNT nor RDX undergo chemical reaction in the presence of fuel oil and/or solvents but act simply as solids in solution. A test to determine if TNT would plate out in solution over time was conducted as well. Plating was observed during this 6 month long test; however, the plating was only a thin layer which presented no hazard when removed with warm acetone. Plating of TNT in current tests will be prevented by frequent feed system washing with warm acetone.

TABLE 2: Viscosity (in centistokes) of TNT Supplemented Fuel oils at Various Concentrations

	TNT (g/100 ml Fuel Oil)			
	0	10	15	20
No. 2 Fuel Oil at 38 °C	3.7	4.2	4.4	4.7
	TNT (g/100 ml Fuel Oil)			
	0	10	20	30
No. 5 Fuel Oil at 60 °C	37.0	56.0	75.0	106.0

Pilot Testing Using a Prototype Combustor

In 1987 a pilot scale (300 kW) combustor was operated using fuel oil supplemented with TNT, RDX and Comp B.⁹ Testing was conducted at the Los Alamos National Laboratory. Mechanical problems with the equipment precluded completion of this test program but not before sufficient data were acquired to show that the use of explosives as fuel supplements was possible. The problems encountered consisted of the failure of the insulation used in the reducing section of the prototype combustor and the failure of the burner tip caused by RDX accumulation and subsequent burning. Enough data were taken to warrant a continuation of the pilot scale testing with careful attention given to selection of a combustion chamber and the feed system used to introduce the explosive supplemented fuel oil. A diagram of the prototype combustor is shown in Figure 3.

In addition to showing the feasibility of utilizing explosive supplemented fuels, stack emissions data were obtained from the prototype combustor. These data were collected and reported by the Army Environmental Hygiene Agency⁴. As only four data runs were performed in which stack sampling was conducted, only generalized conclusions could be reached. The first conclusion is that destruction and removal efficiencies (DRE) of 99.999 % were obtained for TNT combustion. Carbon monoxide and

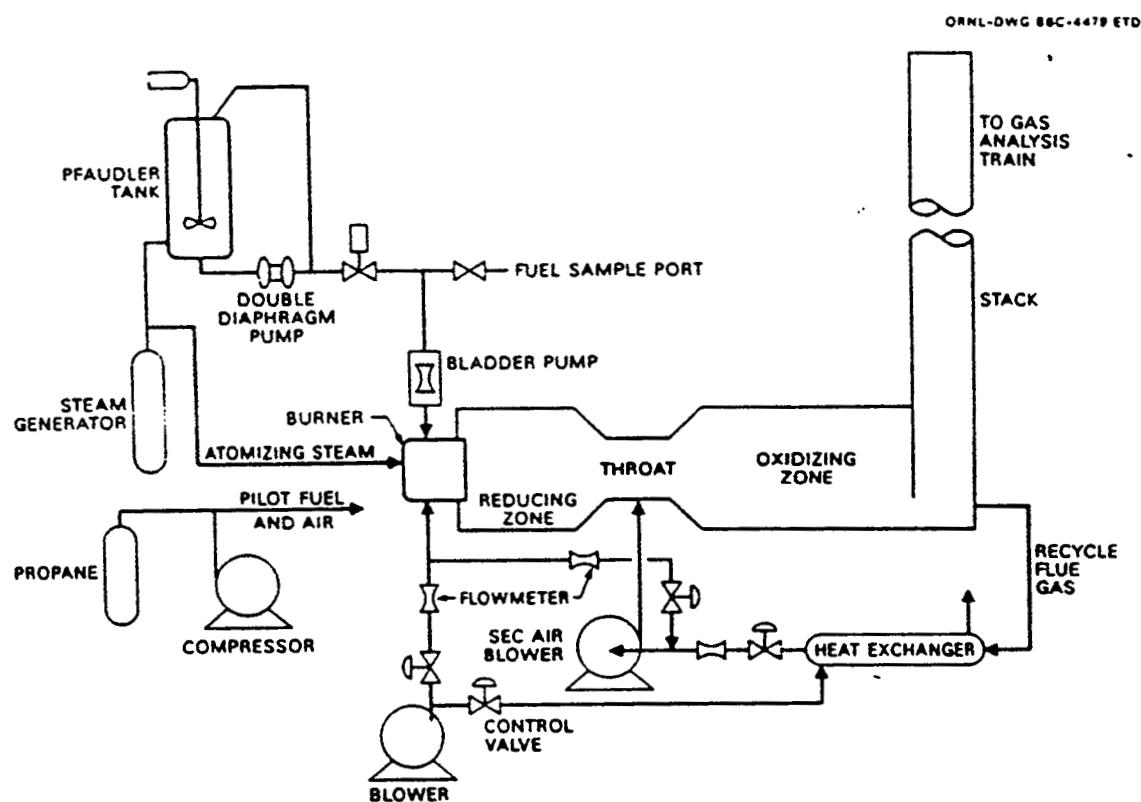


Figure 3: Prototype Combustor Used in Initial Pilot Scale
Studies⁹ 1181

particulate emissions were described as controllable. Finally, and perhaps most important, increased NOx concentrations were found to be caused by the addition of the explosives to the fuel oil. With the limited number of data points obtained and the poor condition of the combustor it is premature to formalize estimates of NOx production for design of control equipment. It should be noted that the NOx emission rate was reported for total NOx as NO₂. For the two data points obtained during supplemented fuel burns, the total NOx emission rate was between 0.50 and 0.56 g/MJ. Methods to curtail this production rate as well as obtain definitive data to support design of abatement systems are key factors in current test plans.

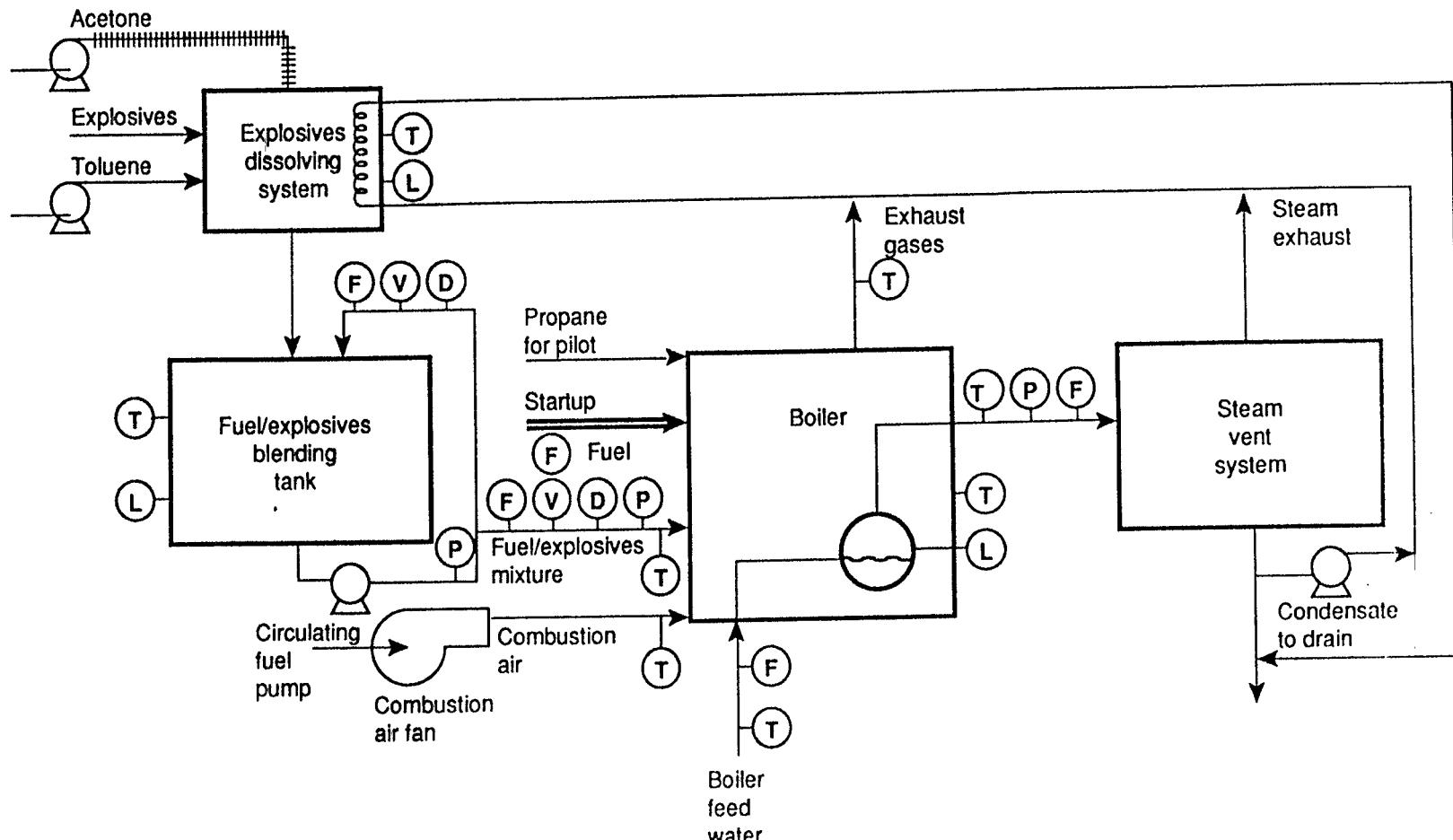
Current Program

Using the foregoing information, USATHAMA's current program was developed to provide the data needed to specify requirements for a complete supplemental fuel system utilizing TNT or Composition B. Testing is scheduled to begin in June 1990. Three major items required engineering design and specification to obtain a working pilot system: (1) a boiler system which would approximate the anticipated full scale boilers that the supplemented fuels would be used in, (2) a system to safely mix and feed the explosives, solvent and fuel oil

was needed which could safely mix and deliver the supplemented fuel, and, (3) a data acquisition plan was needed to obtain the necessary design information for both emission control design, the operating parameters for the burner and preliminary data needed for regulatory approval. A block diagram of the test system is shown in Figure 4.

The boiler is the central piece of equipment in the utilization of explosives supplemented fuels. The majority of currently installed oil burning Army steam boilers are of a water tube design. Various burners and nozzles are used. For the current tests, air atomization was selected to reduce the potential for flashing of the toluene in the supplemented fuel mixture. The boiler selected is designed for 47 boiler horse power and utilizes fuel at an input rate equivalent to 498 kW. A scale factor of ten would include the majority of process steam generation boilers in use today. Larger systems are used; however, more complex burner designs and fuel feed systems would likely require additional testing prior to use of supplemented fuels in these systems. This testing would likely include surrogate fuel mixtures synthesizing the viscosity and heating value of the supplemental fuel.

The second required piece of equipment for this test program is the mixing/feed system. This unit is currently in the design stage and will include provision



- Temporary operation used during startup
- Temporary operation following test run
- (T) Temperature measurement
- (P) Pressure measurement
- (F) Flow measurement
- (L) Level indicator
- (V) Viscosity measurement
- (D) Density measurement

Figure 4. Block Diagram of Supplemental Fuel Pilot Scale System.

for dissolving the explosives in a separate solvent tank, followed by remote addition of this solution to a fixed quantity of fuel oil. The system will mechanically agitate the fuel mixture as well as recirculate the mixture through the piping system. Once a test is completed (by exhaustion of the supplemented fuel mixture), the system will be flushed with acetone by remote control. The mixing/feed system would constitute the primary capital cost for implementation of a system to utilize waste explosives. Care in terms of scalability by utilizing standard equipment in the pilot scale design will assist in the scale up of this unit to a full production system.

Finally, the data acquisition plan was designed to obtain the necessary information for implementation of this technology. This includes flow properties of the selected feed mixtures, efficiency of explosive destruction within the system, heat balances over the system and measurement/characterization of emissions from the system. Eighteen total tests will be conducted. The sample matrices for supplemented fuel experiments are shown in Figure 5 and the expected test sequence is shown in Figure 6. In addition to the 14 tests shown in Figure 5, three tests will be performed using No. 2 fuel oil without the addition of explosives and one test will be performed as a duplicate test using supplemented fuel oil.

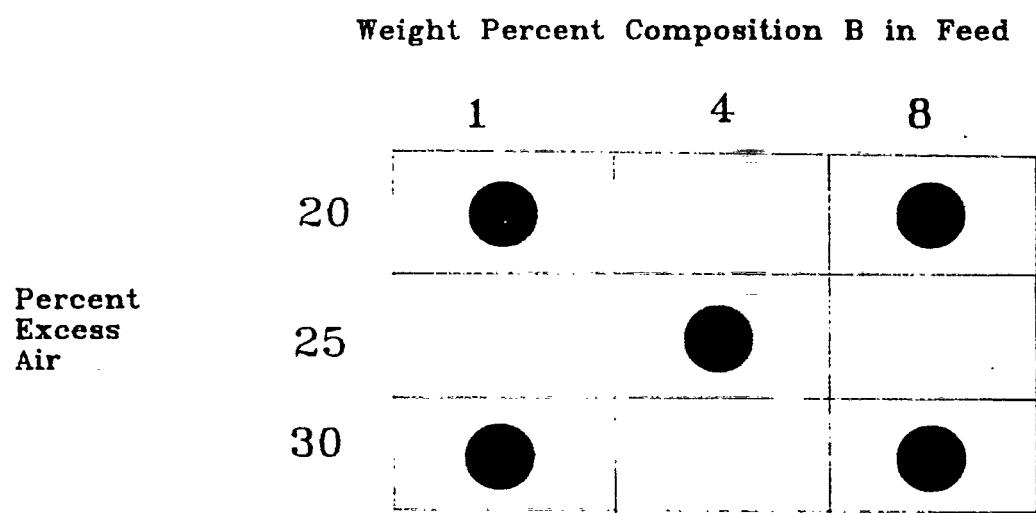
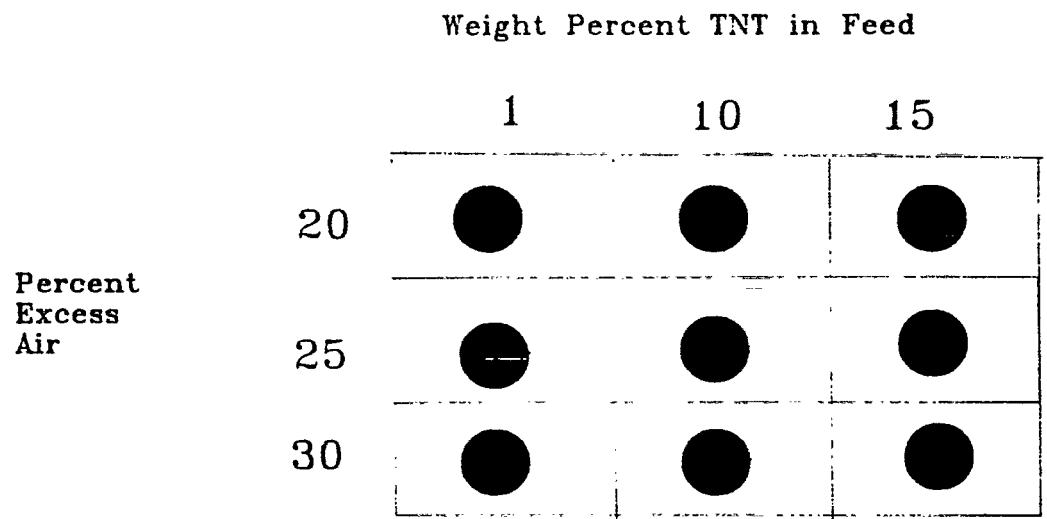


Figure 5: Test Matrices for TNT and Composition B Supplemented Fuels Pilot Scale Testing

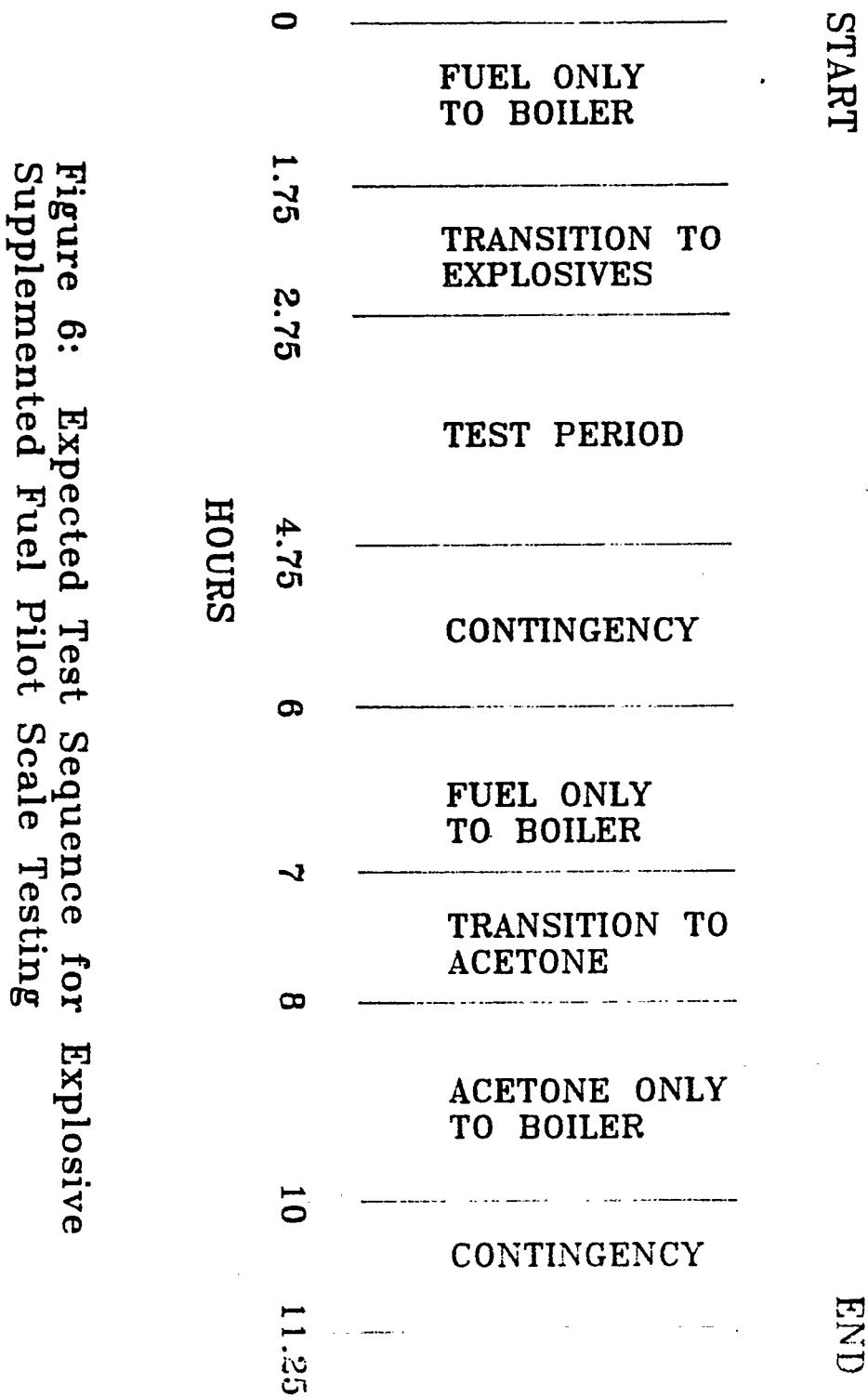


Figure 6: Expected Test Sequence for Explosive Supplemented Fuel Pilot Scale Testing

Detonation Testing

Finally, testing of the detonation characteristics of supplemented fuel oil was conducted.⁷ Both static and dynamic tests were performed. Static tests were conducted in a horizontal .0504 m (2 inch, sched 40, 304 SS) pipe in which the explosive supplemented fuel was allowed to settle for a duration of 4 to 8 hours. Dynamic tests were conducted in a vertical pipe of the same diameter in which the mixture was agitated and then immediately tested for detonation potential. Single phase TNT-acetone-No. 2 fuel oil mixtures showed no propagation of detonation characteristics in static tests at TNT concentrations up to 78 wt percent. TNT-toluene mixtures showed no propagation in both static and dynamic tests at up to 65 wt percent TNT. RDX on the other hand did result in propagation of detonation for static testing at 5.3 wt percent. This was due to RDX particles settling and forming a trail on the bottom of the pipe. For dynamic testing, RDX concentrations up to 15 wt percent did not exhibit propagation of detonation. Supplemented fuels containing less than the concentration required to support propagation of detonation in the static mode will be used in testing.

Conclusion

The use of waste explosives as supplements to fuel used in steam boilers appears to be a viable means of using for fuel what would otherwise be a difficult to dispose of waste product. Previous work has shown the feasibility of using waste explosives as fuel supplements in terms of safety, hazardous waste elimination and cost. Current project plans are aimed at providing the necessary information to make this technology available for implementation at Army installations. By eliminating a hazardous waste through utilization of its energy potential, effective use is made of what is otherwise a costly environmental problem.

REFERENCES CITED

1. Threshold Limit Values and Biological Exposure Indices for 1988-1989, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1988, pg. 37.
2. Military Explosives, Department of the Army Technical Manual TM 9-1300-214, September, 1984, pg. 8-72.
3. IBID, pg. 8-30.
4. Stationary Air Pollution Source Assessment No. 42-21-0515088, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, Maryland, January 1988, pg. 15.
5. Lackey, M.E., "Utilization of Energetic Materials in an Industrial Combustor", U.S. Army Toxic and Hazardous Materials Agency, Report No. AMXTHE-TE-TR-85003, Aberdeen Proving Ground, Maryland, June 1985, pg. 3.
6. IBID, pg. 2.

7. Lackey, M.E., "Testing to Determine Chemical Stability, Handling Characteristics, and Reactivity of Energetic-Fuel Mixtures", U.S. Army Toxic and Hazardous Materials Agency, Report No. AMXTH-TE-CR-87132, Aberdeen Proving Ground, Maryland, April 1988.

8. IBID, pgs. 7-8.

9. Bradshaw, W.M., "Pilot-Scale Testing of a Fuel Oil-Explosives Cofiring Process for Recovering Energy from Waste Explosives", U.S. Army Toxic and Hazardous Materials Agency, Report No. AMXTH-TE-CR-88272, Aberdeen Proving Ground, Maryland, May 1988, pg. 12.